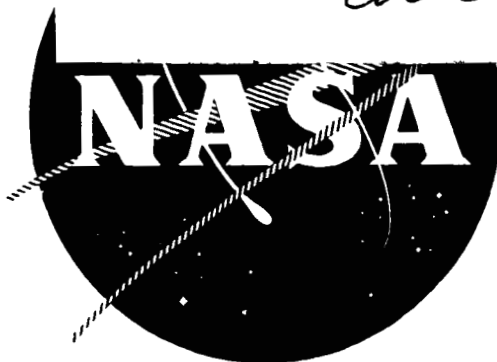


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# SOLUBILITY AND DIFFUSION STUDIES IN ALKALI METALS

THIRD QUARTERLY REPORT

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## ATOMICS INTERNATIONAL

a division of North American Aviation, Inc.

**SOLUBILITY AND DIFFUSION STUDIES OF ULTRA PURE  
TRANSITION ELEMENTS IN ULTRA PURE ALKALI METALS**

**Third Quarterly Report  
(December 29, 1963 – March 28, 1964)**

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**Prepared for  
National Aeronautics and Space Administration  
Lewis Research Center**

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**ATOMICS INTERNATIONAL**

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## REPORTS ISSUED ON THIS CONTRACT

AI-9151, R. L. McKisson, R. L. Eichelberger, and J. M. Scarborough,  
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 Elements in Ultra Pure Alkali Metals," First Quarterly Report,  
 November 6, 1963.

AI-64-5, R. L. McKisson, R. L. Eichelberger, and G. R. Argue,  
 "Solubility and Diffusion Studies in Alkali Metals," Second  
 Quarterly Report, February 7, 1964.

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SOLUBILITY AND DIFFUSION STUDIES OF ULTRA  
PURE TRANSITION ELEMENTS AND COMPOUNDS IN ULTRA PURE  
ALKALI METALS

by R. L. McKisson, R. L. Eichelberger  
G. R. Argue and J. M. Scarborough

I. INTRODUCTION

The purposes of this study are: 1) to define the solution process and determine the equilibrium solubility of highly purified transition metals and selected compounds in highly purified liquid alkali metals, and 2) to measure the diffusion of transition metals and constituents of selected compounds in highly purified liquid alkali metals. The material combinations which are to be considered for both the solution and diffusion studies are: iron, niobium, tantalum, molybdenum, tungsten, zirconium, rhenium, vanadium, hafnium, beryllium oxide, niobium monoxide, tantalum monoxide, zirconium dioxide, zirconium carbide, vanadium monoxide, oxygen-saturated zirconium, and oxygen-saturated hafnium with liquid potassium, and niobium and beryllium oxide with liquid lithium. Specific combinations from the above list will be selected, and it is expected that some combinations will not be investigated.

The studies to be made include the measurement of solubility in the alkali metal at temperatures up to 1200°C, coupled with the investigation of the rate-controlling step and its energy of activation; and the measurement of the liquid state diffusion rate and its energy of activation, also to 1200°C.

It is the goal of this study to develop solubility and diffusion data for well-characterized experimental systems, in which the number and range of complicating variables are minimized, in the hope that such data will not only further

the understanding of these processes in alkali metal systems, but will also be of use in the materials selection and design of space electrical power system components.

This program is divided into the six self-explanatory tasks listed below:

- Task A. Environmental Test System Design and Procurement
- Task B. Material Procurement and Characterization
- Task C. Auxiliary Equipment Design and Procurement
- Task D. Chemical Analysis
- Task E. Experimental Testing and Data Analysis
- Task F. Program Coordination

## II. SUMMARY

The fabrication of the environmental test system is 90% complete, and delivery is scheduled for mid-April.

The outgassing furnace and the first test capsule furnace are assembled and are undergoing mock-up testing to ensure smooth operation.

The auxiliary equipment items which have been delivered are: the electron beam welder, the RYE manipulators, and the control set-point units. The remaining major items to be delivered in April include the step-down transformers, the multipoint recorder, the silicon-controlled rectifier unit, the control signal amplifier, the potassium purification assembly, and the auxiliary high vacuum system.

Two single crystals each of niobium, molybdenum, and tantalum have been received from Materials Research Corporation. The one single crystal of molybdenum received from Metals Research, Ltd. had a flaw and was returned. Metals Research, Ltd. is scheduled to provide us with three single crystals each of niobium, molybdenum, and tantalum during April. Three super-purity polycrystalline iron samples are scheduled for delivery from Materials Research Corporation in April.

The double layer capacitance method (DLC) has been shown to be capable of giving reproducible values of refractory metal surface areas, and will be used in the test program.

Chemical analyses techniques for determining the impurities in sample materials have been tested using the best materials available. In many cases, the procedures are capable of determining lower levels than are present in the best available sample materials.

### III. TECHNICAL PROGRAM

#### Environmental Test System

The purchase order for the design and construction of the environmental test system was placed with the D. L. Herring Corporation in late December. The system under construction consists of five sequentially connected stainless steel vacuum chambers, each with its own pumping system, and separated by vacuum gate valves. The system being constructed is described in some detail in the earlier Quarterly Reports.<sup>(1,2)</sup> Herring's design studies led to the system lay-out shown in Figure 1.

The fabrication of parts was begun in February. Figure 2 shows a number of the machined parts in various states of assembly. Figure 3 shows three chambers with bottoms attached and ready for installation of the penetrations. Figure 4 shows one of the chamber covers with the cooling coils attached and with the protective cover plates over the finished flanges. Figure 5 shows two of the high-vacuum system sub-assemblies each consisting of a 6" NRC oil diffusion pump (Model HS6-1500), a NRC water baffle (Model HW-6, 0318-6), a NRC liquid nitrogen trap (Model HN-6, 0315-6), and a General Technology Corporation SVS-61 manually operated stainless steel valve.

The construction of the environmental test system is now about 90% complete. The chambers have been fabricated, and their interior surfaces electropolished.

Figure 6 shows chambers which are undergoing a vacuum checking prior to being delivered to Atomics International for final acceptance testing. It therefore appears that there will be no difficulty in meeting the presently quoted shipping date of April 15, 1964.

There may be a minor problem in that the three CVC Type SR-75 rotary seals for use in Chamber No. 2 have not yet been delivered to Herring. However, delivery is expected by April 15, 1964. This timing will not adversely affect the acceptance check-out schedule.

The twelve RYE Controls manipulators (Model MIHT) have been delivered and have undergone acceptance testing. One of these has been returned to the supplier for replacement of a faulty seal. The others easily hold a vacuum in the  $10^{-7}$  Torr range, even when being operated. Two of these manipulators are shown in Figure 7.

The electron beam welding unit to be installed in Chamber No. 2 is a 6 KW, 30 KV unit (Model 1615.10) and was procured from the Brad Thompson Industries. This unit has been delivered, and is ready for installation upon delivery of the Environmental Test System.

#### Material Procurement, Preparation, and Characterization

Sample materials are being received. Twenty-five pounds of high purity potassium has been delivered from Mine Safety Appliance Research Corporation. No analyses have been performed on this material. Analyses are planned, however, when the potassium purification unit and the associated transfer equipment is set up so that the metal can be handled without danger of contamination. The analysis provided by MSA is given in Appendix A.

Ten pounds of lithium have been received from Foote Mineral Company. No analysis has been attempted, but the analysis given by Foote is shown in Appendix B.

Two triple pass zone-refined single crystals of each of the metals molybdenum, tantalum, and niobium have been received from MRC Manufacturing Corporation. All of the crystals were of the required 3-inch length, but the tantalum crystals have a marked bow, and one of the molybdenum crystals has a necked region. A telephone inquiry was made of the supplier and we were informed that the delivered tantalum crystals were typical products of present-day technology, and an exchange of crystals would not solve the problem of the bowing in the 3-inch lengths. In order to compensate for this crystal condition, it will be necessary to reduce the crucible I.D. dimension specifications for the tantalum crucibles. The supplier's analyses of these crystals are given in Appendix C.



One single crystal of molybdenum has been received from Metals Research, Ltd., and was found to have a radial pin-hole about 0.060 inches deep near its midpoint. Because this precludes our using it for single crystal crucible fabrication, it was rejected and returned to the supplier. The Metals Research order calls for delivery of three each triple-pass zone refined single crystals of molybdenum, tantalum, and niobium. Their shipping dates are given as March 20 and April 3.

A purchase order is being negotiated with the Sifco Metachemical Division of the Steel Improvement and Forge Company, Cleveland, Ohio, for the preparation of crucibles from our single crystal refractory metals using their electrochemical machining process. Upon completion of our chemical removal of the cut ends of the single crystals, they will be delivered for machining. The ends of the crucibles are presently being deeply etched to remove the material in the vicinity of the cut, and to obtain sample material upon which analyses for metallic impurities can be made.

Further studies of the double layer capacitance (DLC) method of determining surface areas have been made. This measurement was described in the previous report,<sup>(1)</sup> and the problems of the oxide surface layer and the uncertainty of the true surface area value were discussed. Both of these problems are overcome through the use of an electropolishing technique for preparation of the metal surface. By the proper use of electropolishing techniques, the roughness factor for polycrystalline metal surfaces can be reduced to a known and reproducible value of  $1.1 \pm 0.1$ .<sup>(3)</sup> It is hoped that the application of this technique to single crystal materials will result in an even smaller uncertainty in the roughness factor.

This method has been shown in our laboratory to be satisfactory for area measurement of our single crystal crucible materials. A report on the application of the method is in preparation.<sup>(4)</sup>

In order to become more acquainted with the process, a series of measurements was made on mechanically polished samples. Table I shows the results obtained on highly polished Ta, Mo, Nb, and W.

TABLE I

DLC Values for Mechanically Polished Refractory Metal Samples

<u>Material</u>	<u>Crystalline Character</u>	<u>Apparent Area, cm<sup>2</sup></u>	<u>Capacitance* <math>\mu\text{f}/\text{cm}^2</math></u>
Tantalum	Poly Crystal	0.32	7.2
Molybdenum	Single Crystal	0.22	95
Niobium	Poly Crystal	0.32	11.0
Tungsten	Poly Crystal	0.32	45.5

\*These data were calculated from the C vs. emf curves at their flat parts on the cathodic side of the zero point of charge (ZPC). Measurements on the anodic side are more strongly complicated by oxide formation.

The DLC values for Ta are generally in agreement with literature values, which range from 4.5 to 9  $\mu\text{f}/\text{sq cm}$ .<sup>(5,6)</sup>

Rather high values for DLC were obtained for molybdenum. Because of this, tungsten DLC values were re-determined and are reported in Table I. The DLC values for tungsten given in the previous report (AI-64-5)<sup>(1)</sup> are incorrect because of a decimal error in their computation. They should read 39, 42, 43, and 44  $\mu\text{f}/\text{sq cm}$ , and are therefore in agreement with the present data.

The technique selected for the preparation of purified potassium was described in detail in the first Quarterly Report.<sup>(2)</sup> Equipment designed to carry out the sequence described, i.e., filtering, hot gettering, distillation, purified metal storage and dispensing, is under construction. The assembly consists of five component parts. The first is a filter unit (working capacity 350 cc) in which the potassium will be filtered through a 5 micron stainless steel frit at about 75-85°C. The second unit is a gettering pot containing zirconium foil whose function is to remove traces of oxygen from the

potassium. Its operating temperature will be  $750 \pm 50^\circ\text{C}$ . The third unit is the still pot. This component is sized to provide about 40 sq cm of evaporating surface to ensure an adequate net evaporation rate when operated at a 5-10 Torr pressure level. An oversized area is required to compensate for an expected low evaporation rate coefficient.

The fourth unit is a nominal one-inch diameter fractionating column. Tungsten wire coils or screen, or saddles made of tungsten sheet will be used as packing, and it is expected that the 8-9 inch depth of packing will be equivalent to 3-4 theoretical plates. Reflux control will be effected by a partial condenser. The fifth unit is a combination distillate receiver and sample extruder. It is designed to collect up to 300 cc of product and to deliver it into the test system as a  $3/8$ " diameter extruded slug. The expected completion date for the construction of this unit is April 20, 1964.

#### Auxiliary Equipment Design

The outgassing furnace has been constructed in accordance with the drawing shown in the previous report,<sup>(1)</sup> with the exception that all the ceramic parts not necessary for electrical insulation have been replaced with metal. A review of the optimum operating temperature of this furnace has been made and it appears that  $350 \pm 25^\circ\text{C}$  is an adequate compromise. At higher temperatures (above about  $500^\circ\text{C}$ ), the evaporation of chromium from the radiation shields presents a potential source of contamination of the test parts. At lower temperatures, the lower gas desorption rates require unduly long outgassing times. Figure 8 shows the partially assembled parts which comprise the furnace (before replacement of the ceramic spacers), and Figure 9 shows the assembled unit.

The first test capsule furnace has been assembled in accordance with the drawing shown in the previous report.<sup>(1)</sup> Figure 10 shows the assembled unit. Parts for a second unit are on hand and are being assembled. The parts for the sample quench assembly are under fabrication.

A review and evaluation of power supplies and control equipment for the experimental furnaces has been completed. The furnaces will be powered by separate step-down transformers, delivering a maximum of about 40 volts at 100 amperes. Temperature control will be effected by means of a thermocouple-activated precision set-point unit, containing an adjustable internal Zener diode regulated voltage which is opposed to the thermocouple emf. The difference signal is amplified and used to operate a controller unit which has a variable current output. This variable output is in turn used to control a silicon-controlled rectifier unit which then regulates the duty cycle of the furnace power transformer. Components for this control system are scheduled for delivery by mid-April.

#### CHEMICAL ANALYSES

The analytical chemistry support effort has been directed toward the verification of analytical procedures for determining impurities in niobium, tantalum, molybdenum, and iron.

In general, a procedure is considered verified if 1-10 micrograms of an impurity can be determined in the presence of one gram of the material being analyzed (the matrix). In some cases, the impurity content of the best available material is too high to permit qualification of a procedure in the concentration range of 1-10 ppm. Where this situation prevails, the method must be judged on the basis of performance at higher impurity levels or the matrix material must be purified. Both of these approaches have been used.

Efforts have been concentrated on establishing methods of analysis for the impurities most probably present in the single crystal crucible materials. In practice, samples will be removed from the ends of the single crystal rods by dissolution. A portion of this sample will be analyzed by emission spectroscopy to establish major and minor impurity levels. Due to the limited amount of sample available (~ 2 grams) wet chemical methods will be used for the quantitative determination of selected impurities only.

Methods for determining iron, silicon, and tantalum in niobium have been established. The procedure for titanium has not been tested in the concentration range of 1-10 ppm; however, the procedure is probably adequate. Verification at the lower level will be made if efforts to remove titanium from the matrix material are successful. Sensitivity for 3-10 micrograms in the presence of smaller amounts of niobium has been demonstrated.

It has been shown that 1-10 micrograms of iron and silicon can be determined in the presence of approximately one gram of tantalum or molybdenum. Matrix materials were purified for these tests.

The analysis of iron samples poses no major problems. The determination of manganese, anticipated to be the major impurity in iron, is probably the most difficult analysis. Tests have shown that 1-10 ppm manganese in iron can be determined with adequate sensitivity using the permanganate method. However, some additional work is required to establish optimum experimental parameters.

Table II summarizes the status of the analytical support program.

Equipment for determining oxygen in potassium by the Pepkowitz-Judd amalgamation technique has been set up and tested using sodium containing 20-40 ppm oxygen as the test material. Although the oxygen concentration is higher than that anticipated for the potassium samples, the equipment and procedure appear satisfactory for lower levels of oxygen.

An analysis of the melting point depression technique for determining oxygen in potassium was made. It was found that the theoretical m.p. depression for O in K is  $0.001^{\circ}\text{C}$  per wppm. Measurement of such a  $\Delta T$  by comparing the separately measured temperatures of the "flat" regions of two cooling curves is judged to be infeasible. Further, hydrogen and all other dissolved materials would also depress the m.p., so the analysis when made would be non-discriminatory. It is of interest to note that the  $\Delta$ m.p. effect of H is  $0.016^{\circ}\text{C}/\text{wppm H}$ . The details of the study are given in a report.<sup>(7)</sup>

TABLE II

Status of Analytical Support Program

Major Impurities in Refractory Metals by Wet Chemical Methods

<u>Element Determined</u>	<u>Method (Spectro- photometric)</u>	<u>Matrix (Metal Analyzed)</u>	<u>Status</u>
Iron	O-phenanthroline	niobium tantalum molybdenum	1-10 ppm - can be determined with accuracy and precision better than <u>+10%</u> . Analysis of niobium limited to conc. greater than 30 ppm due to impurity (Fe) in matrix. Procedure satisfactory for lower concentrations. Probably adequate for other metals.
Silicon	molybdenum blue from silicomolybdic acid	niobium tantalum molybdenum	1-10 ppm <u>+10%</u> can be determined. Procedure modified to eliminate Nb interference in Nb matrix. Probably adequate for other metals.
Tantalum	Malachite green (phenylflurone method reserved as alternate)	niobium	1-10 ppm <u>+10%</u> or better
Titanium	peroxide	niobium	Tests limited by titanium impurity (425 ppm) in matrix; however, sensitivity for 3-10 micrograms of titanium in the presence of smaller amounts of niobium has been established.
Manganese	permanganate	iron	Sensitivity is adequate for 1-10 ppm. Optimum experimental parameters need to be established.
Molybdenum	dithiol	niobium	Not tested in present of niobium. Method used routinely for Mo + W in other materials. Sensitivity adequate. Procedure ready for testing.

#### IV. NEXT REPORT PERIOD ACTIVITIES

During the next quarter, the environmental test system will be delivered and put into operation.

During April, delivery of all component items is expected. These will be assembled into the system, and their performance verified.

The major effort will be directed toward initiating experimental measurements on iron and niobium sample materials. Molybdenum and tantalum samples will be readied for testing.

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2. R. L. McKisson, R. L. Eichelberger, and J. M. Scarborough, "Solubility and Diffusion Studies of Ultra Pure Transition Elements in Ultra Pure Alkali Metals," First Quarterly Report, AI-9151, (Nov. 6, 1963).
3. J. L. Connor and H. H. Uhlig, J. Phys. Chem. 61, 402 (1957).
4. G. R. Argue, "Double Layer Capacitance Measurements on Ta, Mo, and Nb," AI-TDR-9773.
5. Brodd and Hackerman, J. Electrochem. Soc. 104, 704 (1957).
6. McMullen and Hackerman, J. Electrochem. Soc. 106, 341 (1959).
7. R. L. McKisson, "Analysis of the Freezing Point Depression Technique of Determining Impurity Content of Alkali Metal," AI-TDR-9404, (March 1964).



Appendix A: Potassium Analysis

Analysis of potassium metal supplied by Mine Safety Appliance Research Corporation. Elements shown as "less than" were not seen on the spectrographic plate.

<u>Element</u>	<u>Analysis,</u> <u>ppm</u>	<u>Element</u>	<u>Analysis,</u> <u>ppm</u>
Fe	35	Ti	< 5
B	< 10	Ni	12
Co	< 5	Mo	< 3
Mn	5	V	< 1
Al	6	Be	< 1
Mg	4	Ag	< 1
Sn	< 5	Zr	< 10
Cu	9	Sr	< 1
Pb	< 5	Ba	< 1
Cr	< 5	Ca	10
Si	< 25	Na	30
O	48*		

\*Analysis by mercury amalgamation technique.

Appendix B: Lithium Analysis

Analysis of lithium supplied by the Foote Mineral Company  
(99.98% Li).

<u>Element</u>	<u>Analysis,</u> <u>ppm</u>	<u>Element</u>	<u>Analysis,</u> <u>ppm</u>
Na	43	Al	10
K	11	Si	10
Cl	30	Ni	10
N	22	Cr	10
Fe	10	Co	10
Ca	10	Cu	10

Appendix C: Single Crystals Analyses

Analyses of single crystals supplied by Materials Research Corporation. For each material, MRC states, "this is a typical analysis obtained on similar material electron beam zone refined in an identical manner."

Niobium crystals

<u>Element</u>	<u>ppm</u>
O	10
N	10
H	0
C	8
Ta	20
Fe	< 10
Si	< 5
Cr	< 5
Mo	20

Tantalum crystals

<u>Element</u>	<u>ppm</u>
O	2.5
N	2.5
H	0.3
C	6
Fe	< 10
Mo	< 10
Nb	< 20

Molybdenum crystals

<u>Element</u>	<u>ppm</u>
C	15
O	4.5
N	1.0
H	0.7
Fe	5

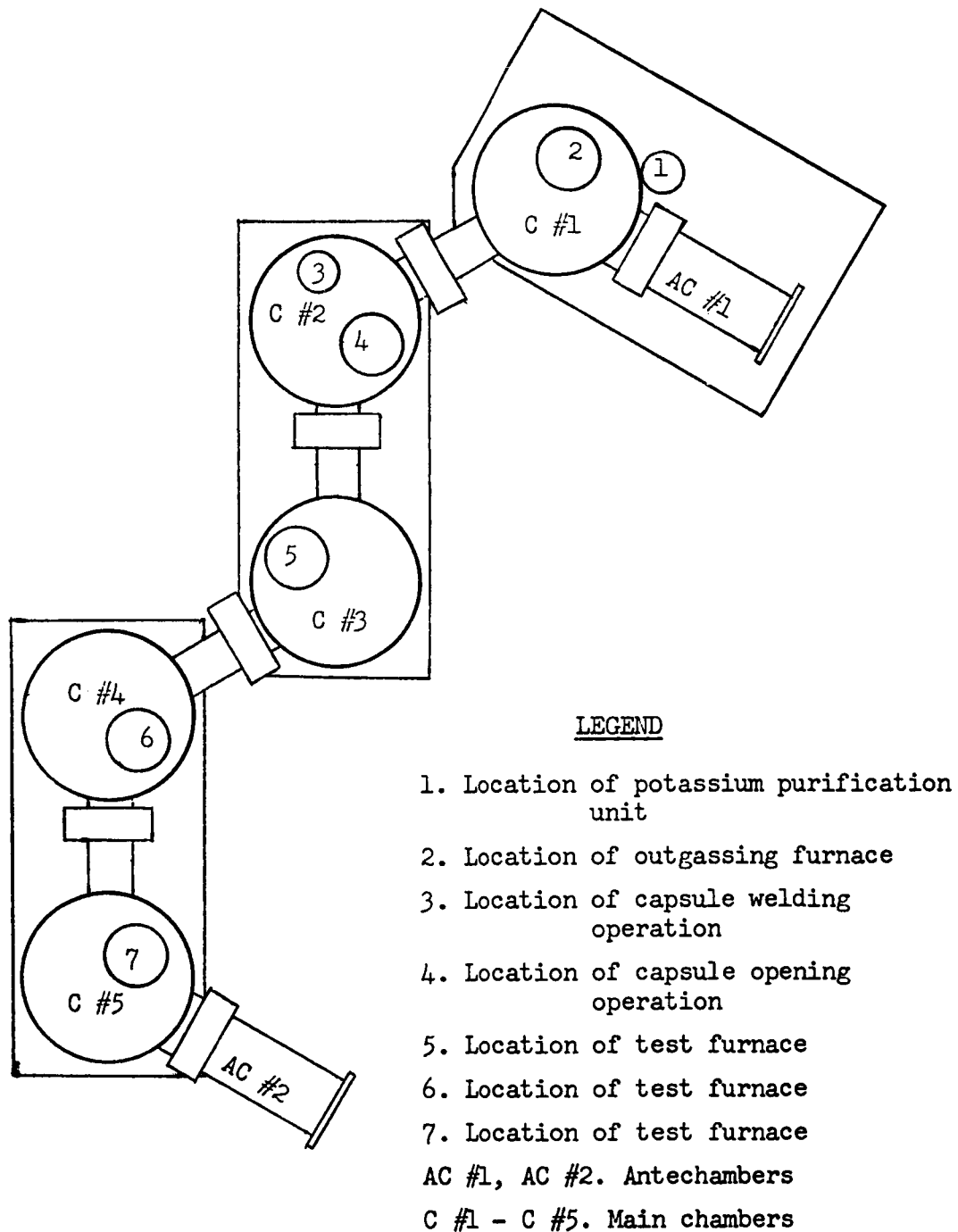


Figure 1. Test Enclosure System Layout Showing the Positions of the Chambers and Selected Components.

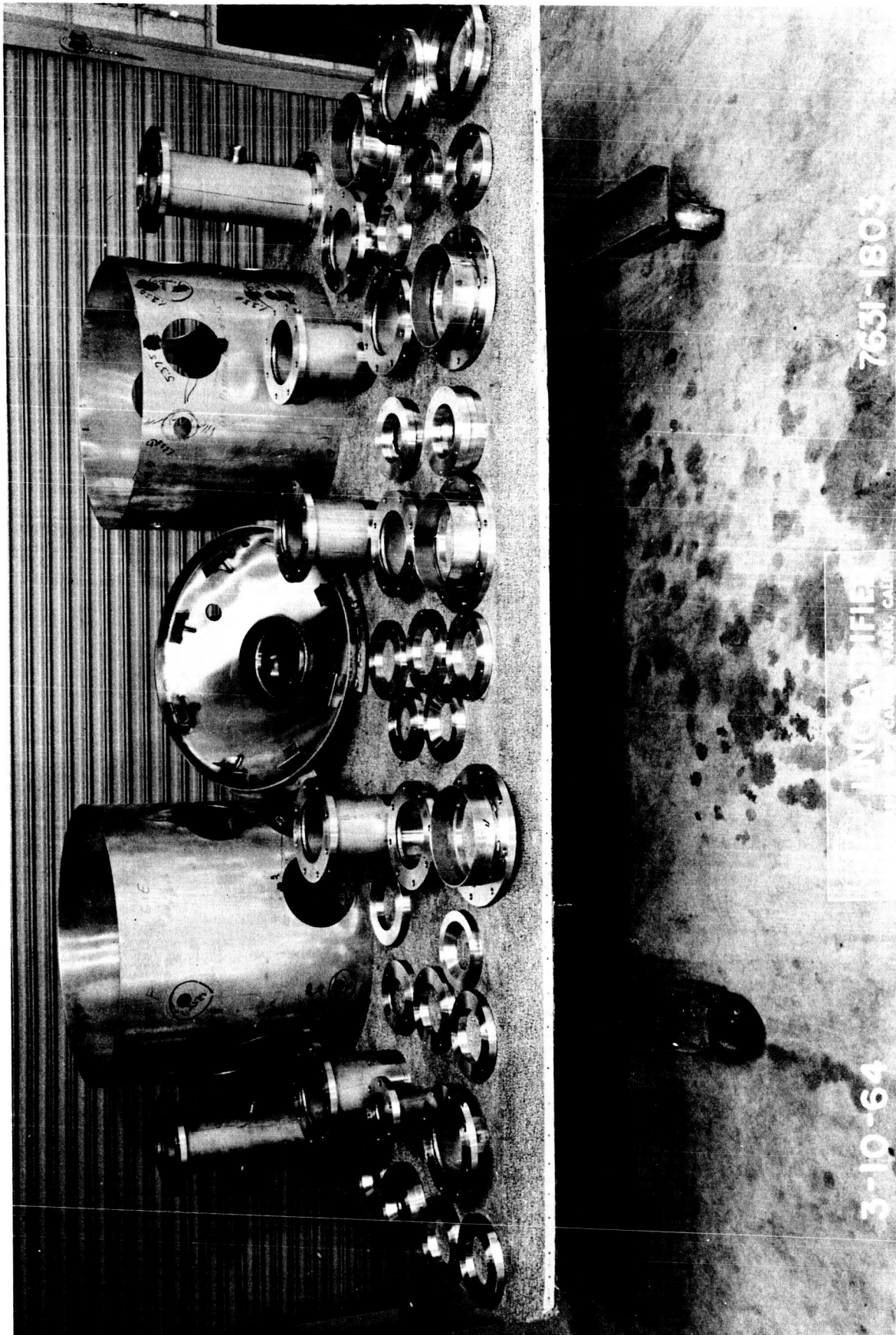


Figure 2. Fabricated Parts for Environmental Test System.

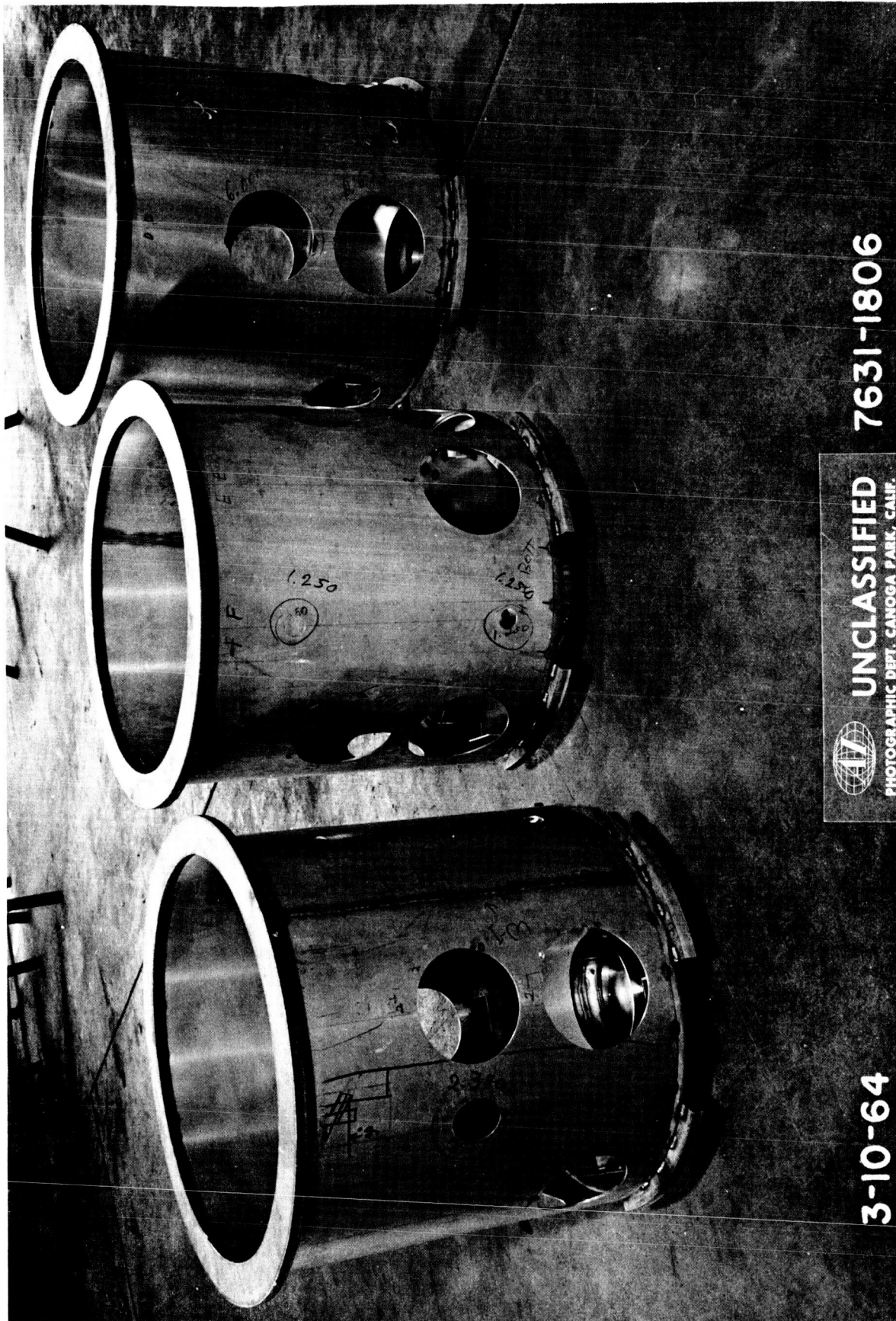


Figure 3. Partially Assembled Chambers for Environmental Test System.



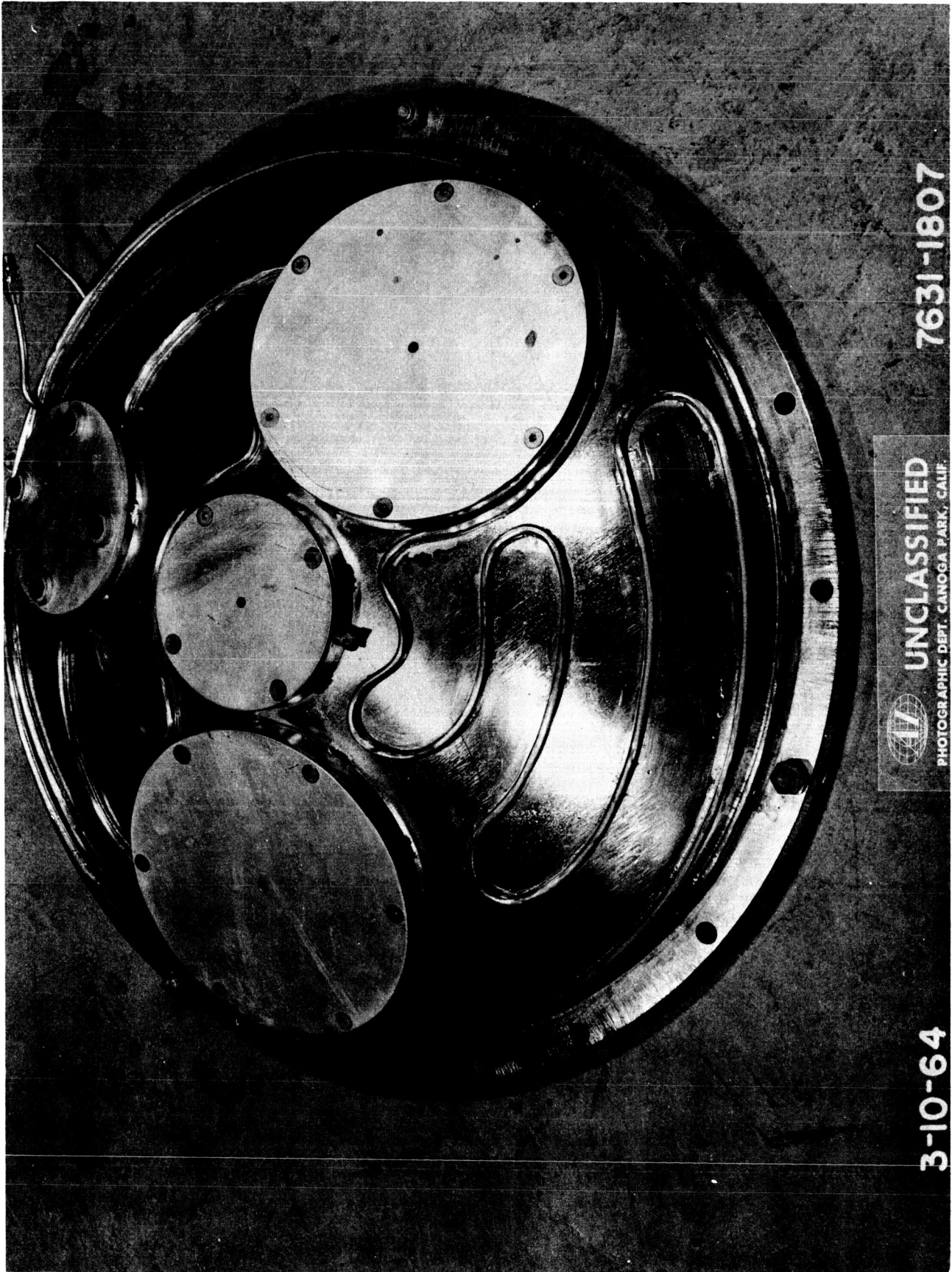


Figure 4. Chamber Cover Showing Cooling Coil Pattern.



Figure 5. Vacuum System Sub-Assembly.



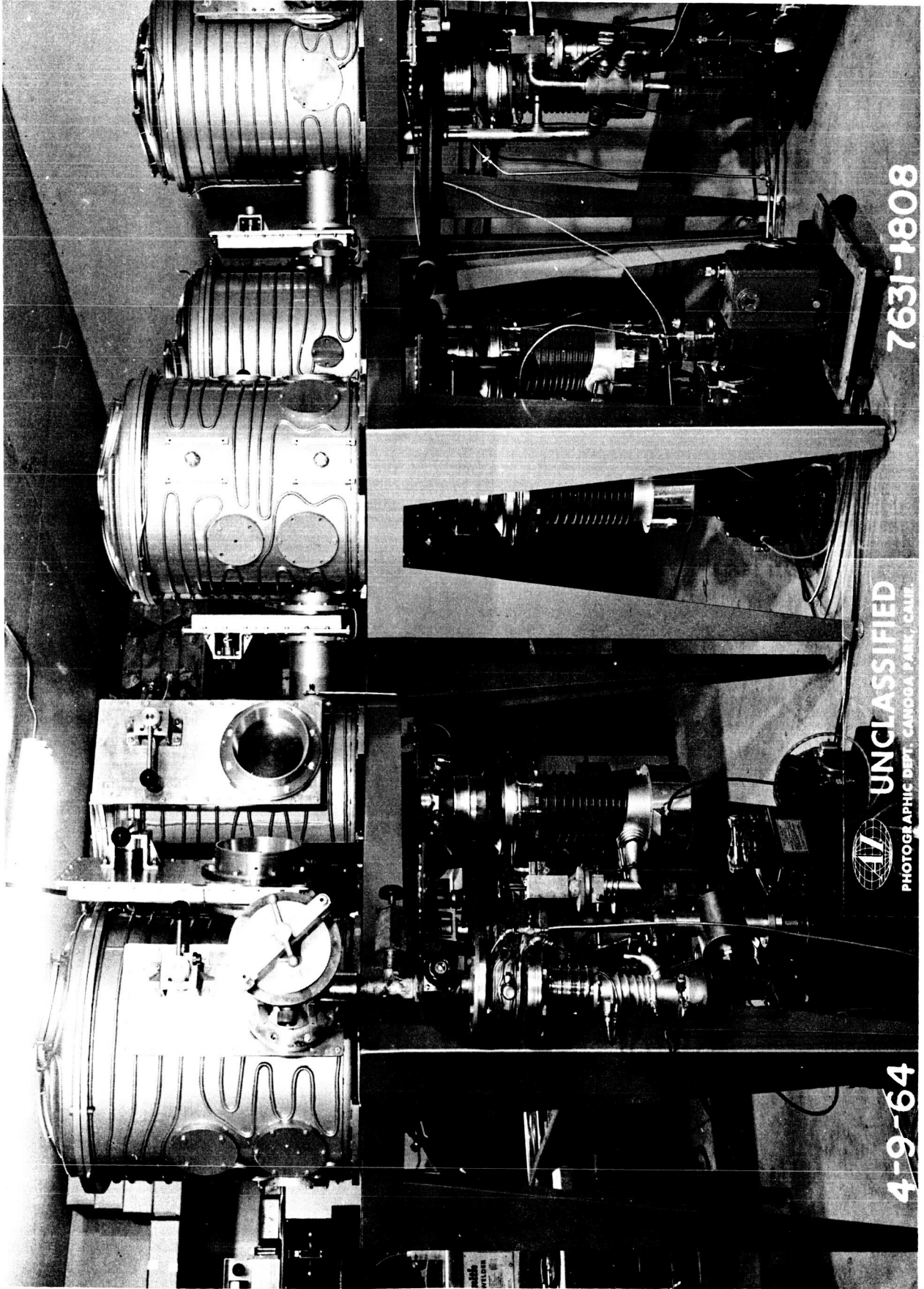
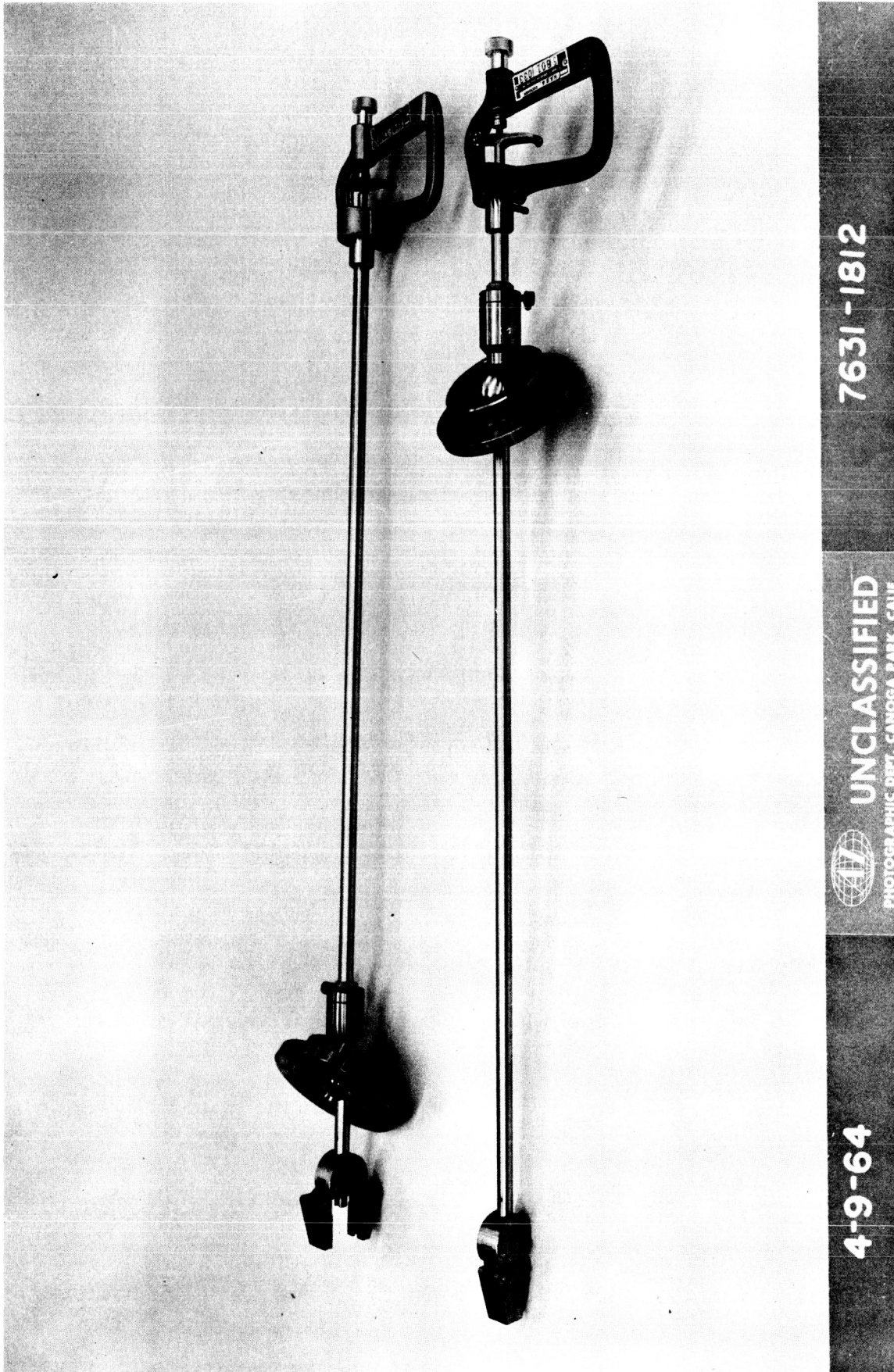


Figure 6. Chambers Undergoing Final Vacuum Checking.



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Figure 7. RYE Controls Manipulators, Model MIHT.

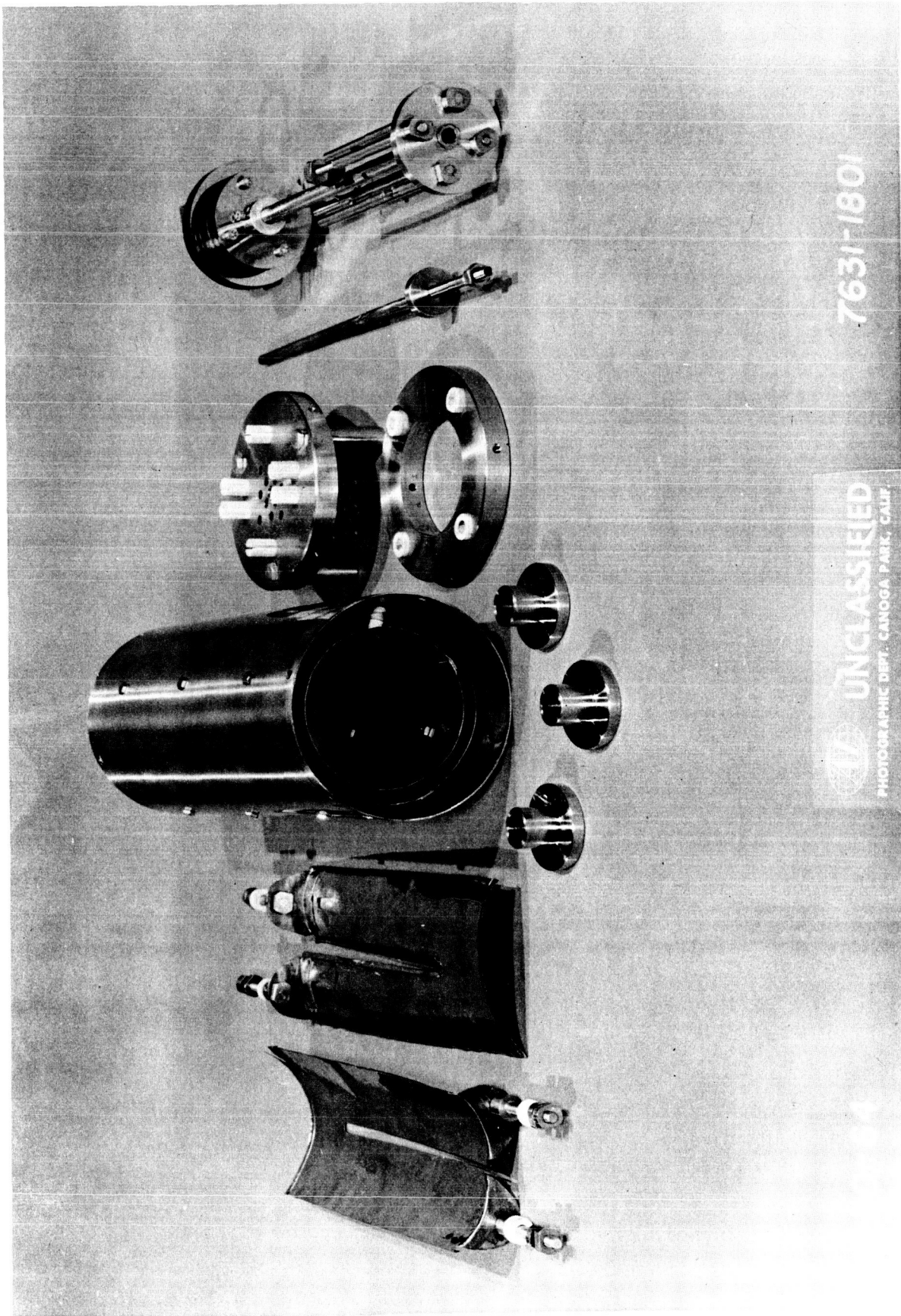
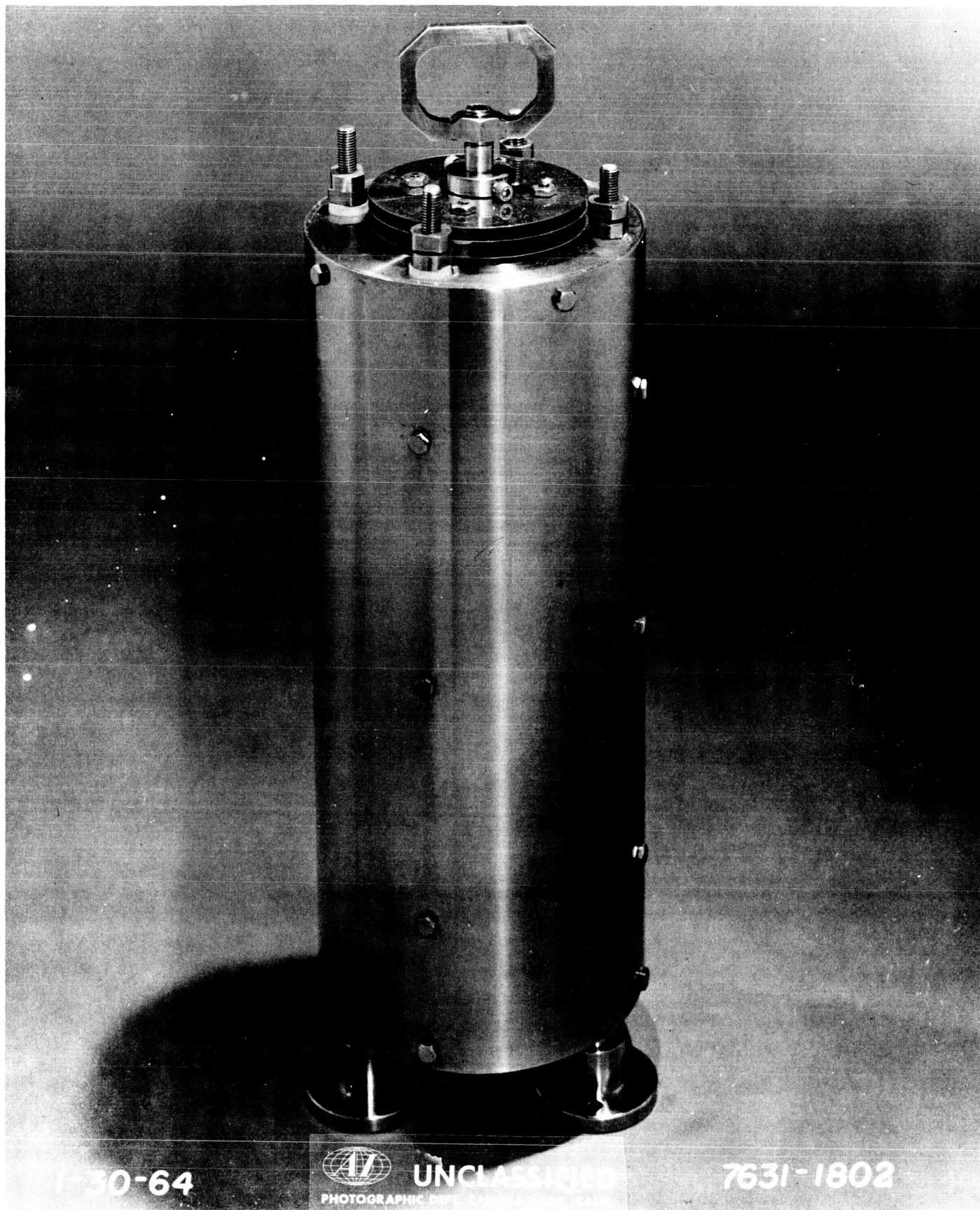


Figure 8. Outgassing Furnace Parts.





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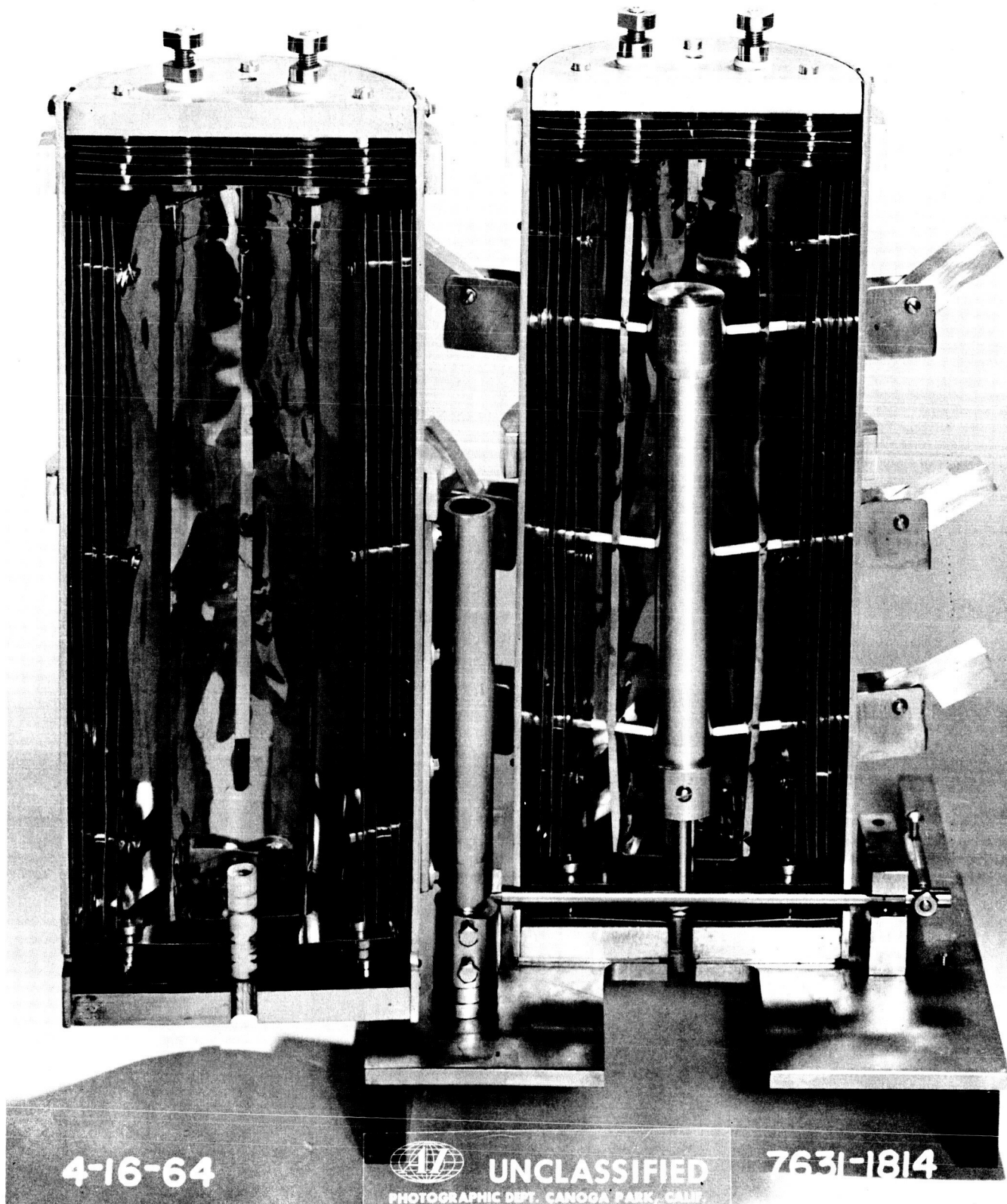


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Figure 9. Outgassing Furnace.



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Figure 10. Test Capsule Furnace.